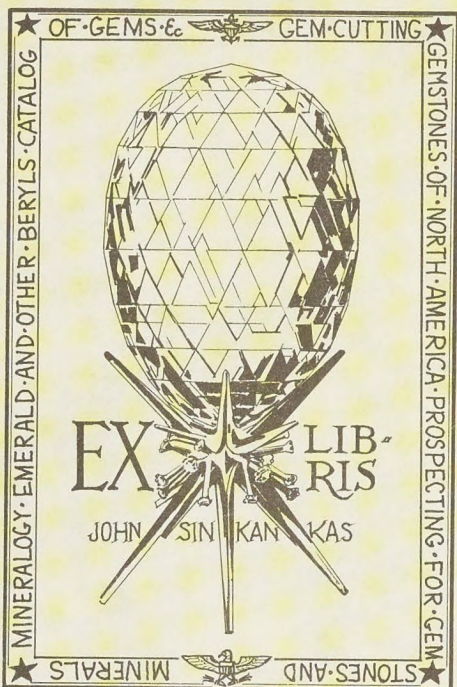


TENNANTITE

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THE IDENTITY OF BINNITE WITH TENNANTITE; AND THE
CHEMICAL COMPOSITION OF FAHLERZ.

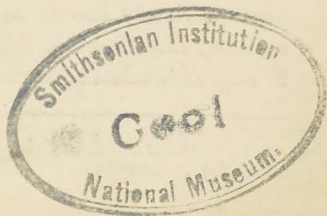
BY

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The Identity of Binnite with Tennantite; and the Chemical Composition of Fahlerz.

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[Read January 31st and June 20th, 1899.]

I. Binnite—(a) Historical and Introductory; (b) Crystallography; (c) Physical Characters; (d) Associations; (e) Chemical Composition; (f) Identity of Binnite with Tennantite.

II. Chemical Composition of Fahlerz.

- (a) Historical and Introductory.
- (b) Tetrahedrite from "Fresney d'Oisans, Dauphiné."
- (c) Tetrahedrite from Horhausen, Rhenish Prussia.
- (d) Tetrahedrite from (Wolfach, Baden)?
- (e) Proposed new formula for Fahlerz.
- (f) Test of new formula by reference to the results of previous analyses.

I. BINNITE.

(a) *Historical and Introductory.*

FEW minerals have had a more varied career than the cubic sulph-arsenite of copper—the binnite of Des Cloizeaux—which as small brilliant crystals is of rare occurrence in the white saccharoidal dolomite of the Binnenthal in Switzerland.

Damour,¹ who first mentioned the crystals, gave the locality incorrectly as St. Gotthard, and supposed them to be the same material as the associated massive sulpharsenite of lead ($2\text{PbS} \cdot \text{As}_2\text{S}_3$), which he analysed and called dufrenoyite. According to Damour's paper the crystals had been previously known as grey copper, and that they were thus early correctly identified it is the object of the present paper to prove. Owing to Damour's mistake there has been much confusion in the names binnite

¹ "Notice sur le sulfo arsénure de plomb de Mont Saint-Gothard (Nouvelle espèce minérale)". *Annales de Chimie et de Physique*, 1845, [iii], XIV, 379-383.

and dufreñoysite, and both of them have been applied to each of the two minerals mentioned above; while, owing to the difficulty of distinguishing the several sulpharsenites of lead from the Binnenthal, the name binnite has had at various times at least four different meanings.¹ The distinctive names cuprobinnite and plumbobinnite, introduced by Weisbach,² have not been generally followed. It may be mentioned here that the other cubic minerals, galena and blende, from the Binnenthal dolomite have sometimes been mistaken for binnite.

The following three analyses have been made of the cubic copper mineral (binnite); they were in all probability made on very small amounts of material, though in only one case is the actual weight given, namely, 0.0785 gram (Stockar-Escher).

	Uhrlaub. ³	Stockar-Escher. ⁴	Macivor. ⁵
Cu	37.74	46.24	46.05
Ag	1.23	1.91	2.43
Fe	0.82	—	—
Pb	2.75	—	—
As	30.06	18.98	18.79
S	27.55	32.73	32.46
	100.15	99.86	99.73
Sp. gr.	4.35—4.69		5.52

From these analyses the following formulæ have been deduced :—

$\text{Cu}_2\text{S} \cdot \text{CuS} \cdot \text{As}_2\text{S}_3$	S. v. Waltershausen, from Uhrlaub's analysis.
$3\text{Cu}_2\text{S} \cdot 2\text{As}_2\text{S}_3$	Rammelsberg (1860) „ „
$3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$	Kenngott, from Stockar-Escher's analysis.
$4\text{CuS} \cdot \text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$	Rammelsberg „ „
$3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$	Petersen (<i>l. c.</i>) „ „

Of these formulæ, the second, $3\text{Cu}_2\text{S} \cdot 2\text{As}_2\text{S}_3$, as deduced from the earliest analysis, is the one usually adopted in the text-books, while the two later and more correct analyses are only mentioned.

¹ Heusser, *Pogg. Ann.* 1855, XCIV, 334. Des Cloizeaux, *Annales des Mines*, 1885, [v], VIII, 398. Kenngott, *Min. d. Schweiz*, 1866, 373. Petersen, *Ber. Offenbacher Ver. f. Naturk.* 1866, VII, 131.

² *Char. Min.* 1880, p. 42.

Sartorius von Waltershausen, *Pogg. Ann.* 1855, XCIV, 120.

⁴ Kenngott's *Uebersicht* for 1856-7, 1859, p. 174.

⁵ *Chem. News*, 1874, XXX, 103. Small amounts of lead and iron were deducted.

These differences are only to be explained by defective analyses made on very small amounts of material, though Trechmann suggested that they might be due to the existence of two cubic copper minerals, the one holohedral and the other tetrahedral. The question as to the holohedral or tetrahedral character of binnite was at one time the subject of much discussion,¹ and it has only recently been decided by Baumhauer² and Trechmann³ that the mineral is really tetrahedral.

The combined crystallographic and chemical results to be described in the present paper show that this much misrepresented mineral, binnite, is nothing more nor less than the arsenical variety of the common fahlerz, and that, except in the more perfect development of the crystals, it does not differ from Cornish tennantite.

The close relationship between binnite and tennantite has been pointed out before. Des Cloizeaux (*loc. cit.*) described binnite as a very arsenical variety of tennantite, but gave the characters which, in his opinion, served to distinguish the two minerals; while Delafosse, in his *Cours de Minéralogie* (1860), actually placed binnite under arsenical grey copper, and pointed out that, according to Stockar-Escher's analysis, it has the composition of Cornish tennantite.

(b) Crystallography.

Previous descriptions of binnite have been based on only a few crystals, sometimes only one. The present description, which however adds very little to those of Baumhauer and Trechmann, is based on the examination of about 60 crystals and the goniometric measurement of 24 crystals and 23 fragments. A large part of this material was collected by Mr. R. H. Solly during blasting operations in the Binnenthal in the summer of 1898.

Crystals of binnite are brilliant in appearance, and most of the faces are very bright and smooth. In size they rarely exceed 3 or 4 mm. in diameter; the largest crystal, which is slightly elongated in the direction of the trigonal axis, is nearly 1 cm. long. They are rich in faces, and two or more forms are usually more or less equally developed (Fig. 1), so that the crystals are rarely distinctly cubic or dodecahedral in habit, whilst only one crystal exhibited a tetrahedral habit. Frequently

¹ Heusser (1856), Sartorius von Waltershausen (1857), Kenngott (1859), Schrauf (1873), Hessenberg (1875), Lewis (1878), Groth (1878).

² "Deutliche hemiëdrische Binnitkrystalle," *Zeits. Kryst. Min.* 1893, XXI, 202-207; *Ibid.* 1897, XXVIII, 545-551.

Min. Mag. 1893, X, 220-228.

the crystals are very irregularly developed, and without removing them from the matrix they are often difficult to decipher unless certain faces can be identified by the characteristic striations and etchings. Even when the crystals are detached they often cannot be properly orientated until two or three zones have been measured on the goniometer, since there is an equality¹ in several of the angles, *e.g.* $100:211=111:110=111:114=35^{\circ}16'$. Usually the crystals occur singly, but sometimes two are grown together in very nearly parallel position. No twinning could be made out.

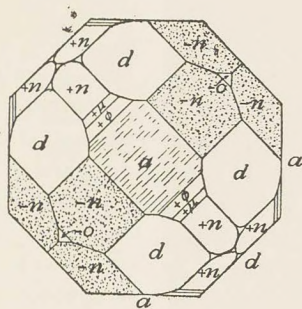


FIG. 1.

The following forms² were identified on the 24 crystals measured on the goniometer:—

- $a\{100\}$. This is present on all crystals either as large or small faces; these are always bright, and are smooth or faintly striated parallel to their intersection with $o(111)$ in the first or positive octant.
- $d\{110\}$. This is present on all crystals usually as a prominent form. The faces are bright and smooth, and only rarely etched and striated parallel to their intersection with the adjacent cube faces.
- $+o\{111\}$. Small and bright; not common. On the single crystal, which is tetrahedral in habit, it is present as a large face striated parallel to its intersections with the cube planes.

¹ See A. Schmidt, "Wiederkehr gleicher Flächenwinkel im regulären Krystall-systeme," *Zeits. Kryst. Min.* 1896, XXV, 477; and *Math. és term.-tud. Értesítő*, 1895, XIII, 331.

² The letters used for the forms are those of Dana (*System of Min.* 18:2, 6th Edit.).

- $-o\{\bar{1}\bar{1}1\}$. This is more frequently present than $+\{111\}$. The faces are small and bright, and often appear to have been developed by the etching of $-n\{2\bar{1}1\}$.
- $+n\{211\}$. Is present on all crystals, and is often a prominent form. It is very bright and smooth, but is sometimes faintly striated parallel to its intersection with $+o\{111\}$, especially when several other $\{hkk\}$ forms are present in the same octant.
- $-n\{2\bar{1}1\}$. Is also present on all crystals either as large or as narrow planes. Usually the faces, though quite even, are dull and like ground-glass in character, giving no reflected image. Rarely they are bright and smooth, or with a slight reddish tarnish. Sometimes the pittings are deep, and light is then seen to be reflected from numerous spots in the position of $-o\{\bar{1}\bar{1}1\}$, and, to a lesser extent, of $d\{110\}$ and $a\{100\}$.
- $+\phi\{611\}$. A small bright face striated parallel to its intersection with the cube; present on most crystals, sometimes rather large.
- $+\{hkk\}$. Some crystals show in the positive octants banded zones of bright narrow faces between the cube and octahedron; they are striated and sometimes rounded parallel to their intersections with these faces. The following angles are a selection of the best of the numerous ones measured on the several crystals, the reflections being from distinct planes:—

	Calcd. to (100).	Meas ^d . (L.J.S.).	(Observers.) ¹
$+\{hkk\}$.			
25.1.1	3°14'	3°18'. Large smooth plane.	—
18.1.1	4 29½	4 28, 4°30'. On two crystals.	—
14.1.1?	5 46	5 40.	—
12.1.1	6 43	6 40, 6°37'.	(Baumbauer, T.).
51.5.5	7 53½	7 53. Fairly large.	—
10.1.1	8 3	8 2, 8°11'.	(Hessenberg, L.T.B.).
911	8 56	8 54.	(Trechmann).
811?	10 1½	9 46, 10°21'.	„
31.4.4	10 20½	10 21.	—
711	11 25	11 25, 11°29'.	(Lewis, T.B.).
611	13 16	13 15, etc.	(Heusser, Groth, L.B.T.).
411	19 28	19 24, 19°28', 19°16', 19°21'.	(Hessenberg, L.B.T.).
311	25 14	25 13, 25°23', 25°12'.	(Trechmann, B.).
322	29 30	29 18.	(Trechmann).
25.12.12	34 10	34 11½.	—
211	35 16	35 16, etc.	(All authors).

¹ T = Trechmann; L = Lewis; B = Baumbauer.

- $+r\{3\bar{3}2\}$. Small bright faces striated or rounded parallel to the edges $[n, n]$, which they truncate. On five crystals.
- $-r\{3\bar{3}2\}$. Small dull faces of the same character as $-n\{2\bar{1}1\}$, the edges of which they truncate; striated parallel to their intersection with $-o\{1\bar{1}1\}$, *i.e.* perpendicular to the edge $[-n, -n]$. On five crystals, but not on those with $+r\{3\bar{3}2\}$.
- $+\Sigma\{552\}$. Small bright faces, sometimes striated and rounded parallel to their intersections with $+o\{111\}$. On four crystals. Besides those from $+r$ and $+\Sigma$, there are other scattered reflections in the zone between (111) and (110) in the rounded positive octants.
- $e\{210\}$. } As bright narrow roundings on the edges formed by the
 $f\{310\}$. } cube and the dodecahedron. $\{210\}$ is new for "binnite."
- $+s\{321\}$. As a small bright face striated parallel to its intersection with $+o\{111\}$. More often as a narrow rounding on the edge $[211, 110]$.
- $+G\{543\}$. } Several small bright planes with curved contours in the
 $+H\{965\}$. } smooth rounded area in the positive octant of one crystal. The faces (211), (965), (543), (332), (453), (695), (121) form a zone. These two forms are new for fahlerz.

	Calcd.	Meas ^d . (L.J.S.)
543 : 453	$11^{\circ}28\frac{1}{2}'$	$11^{\circ}32', 11^{\circ}28', 11^{\circ}32'$.
965 : 695	20 31	20 12.
965 : 332	$10\ 15\frac{1}{2}$	$10\ 10, 10^{\circ}0'$.

From the characters given above, it will be seen that there are several indications of the tetrahedral symmetry, namely:—

- (1). The striation of the cube planes parallel to their intersections with the positive tetrahedron.
- (2). The faces of $+n\{211\}$ and $+r\{332\}$ are bright and smooth in the positive octants, whilst the complementary forms $-n\{2\bar{1}1\}$ and $-r\{3\bar{3}2\}$ are usually dull and rough.
- (3). The development in the positive octants of numerous $\{hkk\}$ forms.
- (4). Hexakistetrahedral forms $\{hkl\}$ occur in the positive octants. Baumhauer's $\{9\bar{4}1\}$ is the only one in the negative octant.

(5). The bright roundings of the edges and coigns in the positive octants, which are sometimes so pronounced that the whole area has the appearance of a polished knob. Only rarely are the crystals rounded in the negative octants.

These points are shown diagrammatically in Fig. 1.¹ It is to be noticed that the hemihedral character is not often apparent from the relative sizes and development of the faces in adjacent octants, and as a rule it seems only to have been brought out by the subsequent etching of the crystals. Thus on some crystals $+n\{211\}$ and $-n\{2\bar{1}1\}$ are of the same size, and are equally bright and smooth, so that the symmetry is apparently holohedral. The effect of the etching has been to roughen the faces in the negative octants, and to round the edges and coigns with bright præsion² planes in the positive octants. Many of the small faces noted above may be only due to præsion.

It should be pointed out that the indications of the hemihedrism given above do not as a rule apply to fahlerz from other localities, as for example those described in Sections II. (b)—(d) below, and that the distinction between positive and negative forms is purely arbitrary, and cannot be compared for different occurrences.

(c) *Physical Characters.*

The colour is iron-black, with a brilliant metallic lustre and an almost velvety appearance. The streak (on paper) is dull and is usually chestnut-brown, but it varies in shade for different crystals, and is sometimes dark brown with a tinge of purple, whilst for two crystals it is black. In the first case the streak on the crystals is cherry-red, and the fine powder is dark purple. Very thin splinters of the crystals with the chestnut-brown streak are translucent and crimson by transmitted light, and crimson flashes may sometimes be seen on the fractured surfaces. The mineral is optically isotropic. Crystals with the black streak are opaque. The colour of the streak appears to depend on the amount of iron in the mineral (p. 192).

A marked feature is the very good and brilliant conchoidal fracture. The mineral is very brittle. $H.=4\frac{1}{4}$. Sp. gr. (weight of 1 c.c.) of the material analysed is 4.62 at 18° (as determined on 0.4378 gram) for the crystals with the chestnut-brown streak, and 4.598 for those with the black streak.

¹ This is much the same as Baumhauer's Fig. 9, Plate IX, in *Zeits. Kryst. Min.* 1897, XXVIII.

² A. Hamberg, *Bihang Svenska Vet.-Akad. Handl.* 1887, XIII (2), No. 4; Abstract in *Zeits. Kryst. Min.* 1889, XV, 84.

(d) Associations.

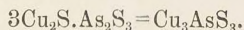
Usually the crystals of binnite occur singly, though sometimes there are as many as a dozen crystals in the same cavity. They seem to be most frequent in those parts of the white saccharoidal dolomite which are veined with coarsely crystalline yellowish dolomite. The crystals rest on the colourless crystallised dolomite lining the cavities, or sometimes on crystals of blende. In one case the crystals of blende and binnite were in very nearly parallel position. Small crystals of pyrites encrust and are partly embedded in the binnite. Sartorite and realgar are frequently present.

(e) Chemical Composition.

The first of the following two analyses was made on eleven of the measured binnite crystals, of which the streak was chestnut-brown. The crystals were broken up, and the fragments carefully selected. The method of analysis was by decomposition in chlorine, as described in the case of andorite.¹ The arsenic was determined in the solution of the volatile chlorides by precipitation with magnesia mixture. The chlorine appeared to have very little action upon the mineral in the cold. The results of the analysis² made on 0.3101 gram were as follows (G. T. P.):

			Atomic ratios.	
Cu	...	49.83	.7895	} 6
Ag	...	1.87	.0174	
As	...	19.04	.2558	1.902
Pb	...	0.17	.0008	0.006
Fe	...	1.11	.0200	0.148
S	...	27.60 ³	.8671	6.446
			99.62	
Sp. gr.	...	4.62		

The numbers correspond approximately to the formula :—



The sulphur is somewhat too high, the atomic ratio calculated to convert the other elements into sulphides being as low as 0.8080.

¹ *Min. Mag.* 1897, XI, 290.

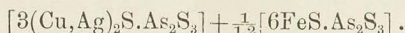
² The atomic weights used throughout this paper are those given by F. W. Clarke (*Smithsonian Miscell. Collections*, 1897, No. 1075).

³ Mean of 27.56 and 27.65, the latter by fusing another portion (0.1972 gram) of the same sample of material with sodium carbonate and potassium nitrate.

A second partial analysis was made on two crystals, of which the streak was black instead of chestnut-brown, in order to discover, if possible, on what this difference of streak depended. The results of the analysis made on 0.1390 gram were (G. T. P.):—

				Atomic ratios.	
Cu	...	44.12	·6991	}	6
Ag	...	4.77	·0445		
As	...	[20.49]	·2690		2.171
Fe	...	3.68	·0662		0.534
S	...	26.94	·8463		6.830
		100.00			
Sp. gr.	...	4.598			

The numbers correspond closely to the formula:—



The results of this analysis, when considered in connection with Rose's analyses of fahlerz (see pp. 204-6), and the three tetrahedrite analyses given in the present paper, suggest that the black streak is due to the presence of iron in larger amount than three per cent., and that the red streak has no connection with the amount of silver (as implied in Dana's *System of Mineralogy*) or with the amount of zinc (as stated in Naumann-Zirkel's *Mineralogie*).

(f) *Identity of Binnite and Tennantite.*

The crystallographic and chemical investigation of binnite, the details of which are given in the preceding paragraphs, shows that neither physically nor chemically is there any essential difference between binnite and tennantite.

The crystals of the Binnenthal mineral possess the same degree of symmetry as the Cornish tennantite, and only differ in their more perfect development, being brighter and richer in faces. W. Phillips,¹ who first described tennantite in 1819, gave the forms: $a\{100\}$, $d\{110\}$, $o\{111\}$, $n\{211\}$ and $\beta\{322\}$; and in the MS. catalogue (by Prof. Miers) of the specimens of Cornish tennantite in the British Museum collection the forms are: $a\{100\}$, $d\{110\}$, $+o\{111\}$, $-o\{1\bar{1}1\}$, $+n\{211\}$, $-n\{2\bar{1}1\}$, $+r\{332\}$, and narrow planes near $+p\{611\}$. All these forms occur on crystals of binnite.

¹ *Quart. Journ. Lit. Sci. & Arts (Roy. Inst.)*, 1819, VII, 95; and Phillips' *Min.* 18:3, 3rd Edit.

The dull crystals of Cornish tennantite are usually much intergrown with each other and with other minerals, so that they do not show the same bright lustre and perfect conchoidal fracture as tinnite. Otherwise the physical characters are the same: thus Cornish tennantite has sp. gr.¹=4.69 and H=4, and shows the same variation in the colour of the streak from dark red to black.

That they are also chemically identical is seen by comparison of the above analyses (pp. 191-2) with the following three analyses of Cornish tennantite:—

	Kudernatsch. ²	Rammelsberg. ³	Wackernagel. ³	3Cu ₂ S.As ₂ S ₃ .	4Cu ₂ S.As ₂ S ₃ .
Cu	48.94	51.62	48.68	52.70	57.60
As	19.10	19.03	20.53	20.72	16.98
Fe	3.57	1.95	3.09	—	—
S	27.76	26.61	26.88	26.58	25.42
	<u>99.37</u>	<u>99.21</u>	<u>99.18</u>	<u>100.00</u>	<u>100.00</u>
Sp. gr.	—	—	4.69	—	—

II. CHEMICAL COMPOSITION OF FAHLERZ.

(a) Introduction.

The chemical formula generally accepted for fahlerz (tetrahedrite and tennantite) and given in the text-books is 4Cu₂S.(Sb,As)₂S₃, or generally 4R''S.R'''₂S₃, where R''=Cu₂,Ag₂,Fe,Zn, &c., and R'''=Sb,As,Bi; the divalent atoms Fe,Zn being supposed to isomorphously replace Cu₂. This is the formula which was originally proposed by H. Rose in 1829, as best expressing the result of seven analyses of fahlerz from various localities made on pure crystallised material.

Very few, however, of the published analyses of fahlerz agree at all closely with this formula, and many of them approach much more nearly to the 3:1 formula 3R''S.R'''₂S₃. One of the latest analyses of tetrahedrite (see analysis 18, p. 213) corresponds to the formula 7RS.2Sb₂S₃ or 4RS.Sb₂S₃+3RS.Sb₂S₃. This want of agreement of most of the analyses with the ordinary text-book formula has received expression in the latest

¹ Wackernagel (1860) and Baumert (1858).

² *Pogg. Ann.* 1836, XXXVIII, 397.

³ Rammelsberg's *Handb. d. Min.-Chem.* 1860, p. 88. Other analyses of Cornish tennantite are given by R. Phillips (1819), Hemming (*Phil. Mag.* 1831, X, 157), and vom Rath and Baumert (*Sitz.-ber. niederh. Ges. Bonn*, 1858, XV, p. LXXII).

supplement (1895) to Rammelsberg's *Mineralchemie*, where the composition of fahlerz is given as a mixture of $3\text{RS.Sb}_2\text{S}$ and $4\text{RS.Sb}_2\text{S}_3$.

It will be found as a general rule that the analyses which approach most closely to the ordinary 4 : 1 formula are those in which the percentages of divalent elements (Fe, Zn) are high. On the other hand, whenever an analysis shows a comparatively simple composition, with only small percentages of divalent elements, the numbers correspond very closely to the 3 : 1 formula. This is the case with the first analysis of binnite (p. 191), and also with the analyses of Cornish tennantite, quoted on p. 193, as is seen by comparing the numbers with those corresponding to the two formulæ $3\text{Cu}_2\text{S.As}_2\text{S}_3$ and $4\text{Cu}_2\text{S.As}_2\text{S}_3$ given on p. 193. Kudernatsch was only able to make his analysis (p. 193 above) accord with the 4 : 1 formula by considering part of the copper to be present as CuS instead of Cu_2S .

The tennantite from Rudelstadt, Silesia, of which the analysis (No. 10, p. 209) corresponds to the 3 : 1 formula, was on that account described by Websky as a new species under the name of "julianite." "Annivite," "studerite," and the more recent "falkenhaynite"¹ are other names which have been applied to fahlerz, of which the analyses accord more nearly with the 3 : 1 than with the ordinary text-book formula. In some of the text-books many of these are referred to the obscure orthorhombic (?) mineral stylotype, to which the formula $3(\text{Cu}_2, \text{Ag}_2, \text{Fe})\text{S.Sb}_2\text{S}_3$ has been assigned.

In the case of tetrahedrite proper the percentage of iron or zinc seldom sinks below 3. An analysis (No. 11, p. 209), however, by Nilson, of the so-called "aphthonite" from Gärdsjö, Wermland, shows only fractional percentages of both iron and zinc. As shown on p. 209, the numbers obtained in this analysis agree almost perfectly with the 3 : 1 formula.

There is thus strong evidence in favour of the view that the true formula for the simple sulphantimonite or sulpharsenite of copper is $3\text{Cu}_2\text{S.}(\text{Sb, As})_2\text{S}_3$. The iron and zinc appear to be the disturbing elements which cause the analyses to approach the 4 : 1 formula of Rose.

In 1870 Petersen, in a short note on the formula of sulpho-salts,² actually proposes the 3 : 1 formula for fahlerz, and suggests that variations from this are due to the presence of impurities such as iron- and copper-pyrites in the material analysed. The well-known intimate asso-

¹ Scharizer, *Jahrb. geol. Reichs.* 1890, XL, 433.

² *Neues Jahrb. f. Min.* 1870, 455-9.

ciation and parallel intergrowth of copper-pyrites and blende with tetrahedrite, as described by Sadebeck, Becke and others, lend some support to this view. The frequent occurrences of tetrahedrite in which the fracture is granular and interrupted, instead of being perfectly smooth and conchoidal, also suggests that most crystals are not homogeneous, but that they are intimately intergrown with copper pyrites, which indeed can in many cases be seen as minute yellow specks throughout the whole material. In choosing specimens for the present analyses, very few were found which were at all suitable for the collecting of pure material.

The idea, however, that the iron in fahlerz is due to impurities of iron- or copper-pyrites is not supported by an examination of the hitherto published analyses. Calculations of the atomic ratios show that, as a rule, the total sulphur found corresponds with the amount calculated to convert the other elements into sulphides, the iron being supposed to be present as FeS and not as FeS₂.

That the sulphides of the divalent metals might be present in fahlerz in another form of combination with the sulphides of antimony and arsenic than the sulphides of the monovalent metals has been advocated by Kenngott in an elaborate paper on the formula of fahlerz.¹ As the result of his calculations of a large number of analyses he was led to propose the general formula $4R'_2S.R'''_2S_3 + x[3R''S.R'''_2S_3]$. He obtained this result, however, by starting with the assumption that the correct formula for the simple mineral was $4Cu_2S.(Sb,As)_2S_3$, and by referring analyses which gave the 3:1 formula to "julianite," which he regarded as a distinct species.

In this state of uncertainty as to the true formula of fahlerz, the present investigation was undertaken in order to see if the analysis of pure tetrahedrite of simple composition would confirm the result obtained in the case of binnite, and substantiate the 3:1 in preference to the generally accepted 4:1 formula; and to discover, if possible, in the case of specimens of more complex character, in what way the iron and zinc enter into the composition of the mineral.

Three specimens from different localities were selected for analysis. These were chosen on account of their comparative freedom from impurities, such as iron- and copper-pyrites, and the apparent homogeneity of the crystals as indicated by the perfectly smooth and brilliant conchoidal fracture. This latter character was the one chiefly relied upon as a guarantee of purity. In the analyses only crystal fragments showing an

¹ Kenngott. "Ueber die Fahlerzformel." *Neues Jahrb. f. Min.* 1881, II, 228-248.

uninterrupted conchoidal fracture were used. The greatest care was taken in selecting material absolutely free from all visible impurities each fragment being picked out under the lens and then examined under a microscope, the 1in. objective of which was fitted with a Lieberkuhn.

(b) *Tetrahedrite from "Fresney d'Oisans, Dauphiné."*¹

This specimen is described in the Heuland sale catalogue for May 3rd, 1833, as: "895. An UNIQUE specimen of grey Copper Ore from Fresney, Oisans, Dauphiné, with Rock-crystals and Carbonate of Iron."

On the matrix is a fine isolated crystal, measuring 4 cm. along the octahedral edge, which is by far the largest and best in the large suite of tetrahedrites in the British Museum collection.

Crystallography.—The two tetrahedra $+o\{111\}$ and $-o\{1\bar{1}1\}$ are equally developed, so that the crystal has the appearance of a regular octahedron (Fig. 2); but while $+o\{111\}$ is bright and smooth, the com-

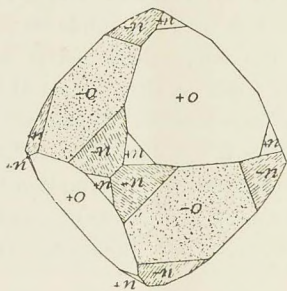


FIG. 2.

plementary tetrahedron $-o\{1\bar{1}1\}$ is dull and rough, being covered with numerous minute triangular pyramids reflecting light with the planes of the rhombic dodecahedron. The only reflections in the positions of the faces of $-o\{1\bar{1}1\}$ are from the small triangular truncations of these pyramids; these small planes are smooth, but rather dull. The two triakistetrahedra, $+n\{211\}$ and $-n\{2\bar{1}1\}$, are well developed; the former is bright and smooth, and very faintly striated parallel to its intersection with the positive tetrahedron; the latter, which is slightly larger, is dull

¹ The authority for this locality is the Heuland catalogue. Two other specimens of tetrahedrite from the Heuland collection, and now in the British Museum, which are exactly similar in appearance and matrix to the specimen now described, are, according to the Heuland catalogue, from Baigorri, Basses-Pyrénées. The latter occurrence is mentioned by Romé de l'Isle (1773), and is described at length by Prof. Lacroix (*Min. de France*, 1897, II, p. 724). Lacroix only just mentions Museum specimens of tetrahedrite as being labelled Fresney d'Oisans.

and deeply striated perpendicular to its intersection with the negative tetrahedron, *i.e.* parallel to its intersection with the rhombic dodecahedron. The rhombic dodecahedron is represented by bright narrow planes truncating the edges $[+o, -o]$, or oscillating with $-n\{2\bar{1}1\}$ and giving rise to the striations on these faces. With the contact goniometer the angle $on = 111 : 211$ was measured as 20° (calculated $19^\circ 28'$).

Physical Characters.—The colour is steel-grey, with bright metallic lustre; the streak is dull and dark brown, with a tinge of purple. The mineral is opaque, even in thin splinters. Fracture conchoidal, and very bright and smooth. Very brittle; $H=4\frac{1}{2}$. Specific gravity of the material analysed 4.921 at 17° .

Associations.—Although the crystal is in places slightly cracked and etched, yet the material is perfectly fresh in appearance. The cracks are filled with films of limonite together with a little malachite and chessylite, and these substances are in places present as films on the surface of the crystal. On the fractured surfaces of the crystal are one or two yellow marks which seem to be films of copper- or iron-pyrites.

The matrix consists mainly of large rhombohedra of chalybite altered to limonite. On this is the large crystal of tetrahedrite, with a small crystal and a little massive tetrahedrite. Of later formation than this are clear colourless prisms of quartz. All these minerals are coated in places with limonite, and this in turn is coated with thin crusts of green malachite and blue crystalline chessylite. After the deposition of: (1) chalybite, (2) tetrahedrite, and (3) quartz, the material seems to have been slightly crushed and the chalybite altered to limonite, followed by an etching and slight surface alteration of the tetrahedrite.

Chemical Composition.—Plenty of pure material for analysis could be collected without difficulty from the fractured surface of the large crystal. Before being picked over, the fragments were boiled in hydrochloric acid to remove limonite and copper carbonates.

The result of the analysis was as follows (G. T. P.) :—

			Atomic ratios.		Calcd. for $3\text{Cu}_2\text{S.Sb}_2\text{S}_3$.
Cu	...	45.39	.7192	6	46.83
Sb	...	28.85	.2414	2.017	29.55
As	...	trace			—
Fe	...	1.32	.0238	.199	—
Pb	...	0.11	.0005	.004	—
S	...	24.48	.7690	6.424	23.62
			<hr/>		<hr/>
			100.15		100.00
			<hr/>		<hr/>
Sp. gr.	...	4.921			

Weight of material used in analysis = 0.6395 gram and (for separate sulphur determination) 0.3672 gram. The atomic ratio of the total sulphur calculated for the sulphides on the assumption that the iron is present as iron-pyrites is .7698.

Deducting the iron and lead as FeS_2 and PbS , the atomic ratios for $\text{Cu} : \text{Sb} : \text{S} = 6 : 2.017 : 6.022$, which correspond almost exactly to the formula $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3 = \text{Cu}_3\text{SbS}_3$.

(c) *Tetrahedrite from Horhausen, Rhenish Prussia.*

The beautiful crystals of tetrahedrite from Horhausen in Rhenish Prussia have been described¹ several times, but the material from this locality does not appear to have been analysed. Since the crystals are so perfectly developed, have a good conchoidal fracture, and are not intimately associated with copper-pyrites, they appeared to form suitable material for establishing the tetrahedrite formula. The specimen selected for detailed examination was the one showing the least amount of blende and no copper-pyrites on the free surface.

Crystallography.—The brilliant crystals have all their faces bright and smooth; they measure up to 5 mm. across, but are usually much smaller.

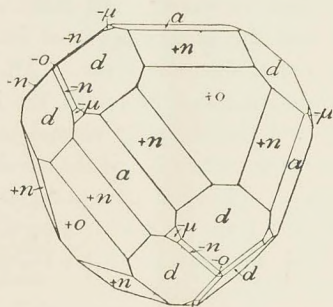


FIG. 3.

The habit of the crystals is tetrahedral, with large faces of the rhombic dodecahedron (Fig. 3). The forms present on six measured crystals giving excellent readings are, in order of predominance:—

¹ C. Klein, *Neues Jahrb. f. Min.* 1871, 493. A. Sadebeck, *Zeits. Deutsch. geol. Ges.* 1872, XXIV, 458. G. Seligmann, *Zeits. Kryst. Min.* 1877, I, 335. G. vom Rath, *Zeits. Kryst. Min.* 1881, V, 258. P. Groth, *Min.-Sammlung, Strassburg* 1878, p. 66.

- $+o\{111\}$. This is usually smooth, but is sometimes represented by bright vicinal faces $\{hhl\}$ ($h > l$) deeply striated parallel to their intersections with o and d .
- $d\{110\}$. Bright and smooth.
- $+n\{211\}$. Bright and smooth.
- $a\{100\}$. Bright and smooth. Faintly striated parallel to its intersection with $+o\{111\}$.
- $-n\{2\bar{1}1\}$. Narrow; not so bright as $+n$, and sometimes rather rough.
- $-\mu\{4\bar{1}1\}$. Bright and smooth; small.
- $-o\{1\bar{1}1\}$. Bright and smooth; very small.
- $+\mu\{411\}$. Observed once as a narrow plane.
- $-r\{3\bar{3}2\}$. Observed once as a very narrow rounding between two planes of $-n\{2\bar{1}1\}$.

The above forms, with the exception of the last two, are present on all crystals, and there is very little variation in the relative sizes of the faces on different crystals. The crystals are sometimes grouped together in more or less parallel position, or small crystals are partly embedded in large ones, but no definite orientation between two crystals could be discovered.

There is no marked difference between the surface characters of the faces in adjacent octants, nor could any difference be developed in attempts to etch the crystals with bromine water or with nitric acid.

Physical Characters.—The colour is iron-black, with brilliant metallic lustre. Streak dark brown with a purplish tinge. Only the thinnest flakes are crimson by transmitted light; the mineral is then seen to be optically isotropic. Fracture conchoidal, bright and smooth, but not quite so good as that of binnite; where the crystals are intergrown close to the matrix the fracture is only sub-conchoidal. Brittle; $H=4\frac{1}{4}$. Sp. gr. of the material analysed 4.969 at 17° .

Associations.—The matrix consists of massive buff-coloured chalybite with milky quartz in veins and patches; it encloses a few specks of copper pyrites and of a black mineral which is probably massive tetrahedrite. On the free surface are the following crystallised minerals in the order of formation: (1) Lenticular crystals of chalybite with one or two quartz crystals. (2) Galena in dull well-developed octahedra, with small cube planes. (3) Tetrahedrite, which has grown over, and is intimately associated with, the galena. (4) A few small crystals of reddish-brown blende.

Chemical Composition.—The material collected for analysis was boiled with strong hydrochloric acid to remove galena before being picked out under the lens and microscope.

The result of the analysis is as follows (G. T. P.) :—

			Atomic ratios.	
Cu	...	41.55	·6582	6
Sb	...	28.32	·2370	} 2.20
Bi	..	0.83	·0046	
As	...	trace		
Fe	..	1.02	·0184	} 0.55
Zn	...	2.63	·0405	
Pb	...	0.62	·0030	
S	...	24.33	·7642	6.95
		99.30		
Sp. gr. ...		4.969		

Weight of material used in analysis 0.4856 gram and (for separate sulphur determination) 0.2803 gram.

The calculated atomic ratio of the total sulphur, assuming iron present as FeS, is .7530. After deducting $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, the atomic ratios of the residue are—

$$\text{Sb} : (\text{Fe}, \text{Zn}) : \text{S} = .2 : .55 : .95,$$

which correspond approximately to the formula $6(\text{Fe}, \text{Zn})\text{S} \cdot \text{Sb}_2\text{S}_3$. The correspondence would have been closer but for a slight loss of zinc during the filtering of the sulphide. The combined formula is therefore :

$$[3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3] + \frac{1}{10} [6(\text{Fe}, \text{Zn})\text{S} \cdot \text{Sb}_2\text{S}_3].$$

(d) *Tetrahedrite from (Wolfach, Baden)*¹?

Crystallography.—The crystals are tetrahedral in habit (Fig. 4), with large $+o\{111\}$, and smaller $+n\{211\}$, $+\mu\{411\}$ and $a\{100\}$; and on the acute trigonal coigns very small bright $-o\{1\bar{1}1\}$ and $d\{110\}$. The faces of $a\{100\}$ and $+\mu\{411\}$ are deeply striated parallel to their mutual inter-

¹ This specimen has been for many years in the British Museum collection, and was labelled "Andreasberg, Harz" by the late Mr. T. Davies, but the associations are so unlike those described in the literature of minerals from the Harz (Luedecke, *Min. d. Harzes*, 1896) that this locality must be considered as doubtful. On the other hand, on account of the remarkable agreement in every particular with Sandberger's (*Neues Jahrb. f. Min.* 1869, pp. 301, 297; *Untersuch. über Erzgänge*, 1885, II, pp. 288, 283) description of tetrahedrite from the Wenzel Mine near Wolfach in Baden, we have ventured to suggest that the specimen in all probability came from this locality.

sections, while the striations on $+n\{211\}$ in the same direction are much less marked. The faces are bright, but are roughened by curious granular and vermiform markings, so that they give poor reflections; besides these minute markings, there are a few larger thread-like elevations, which

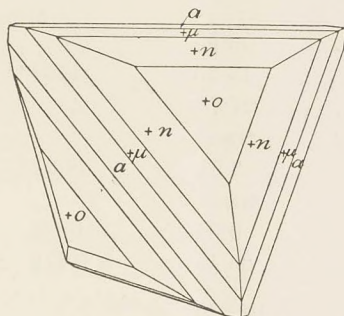


FIG. 4.

often run across from one crystal to another; these suggest healed-up cracks in the crystals. All the crystals are of exactly the same habit and easy to decipher, so that only one was measured on the goniometer. In size the crystals average about 0.5 cm. along the tetrahedral edge, the largest being 1.5 cm.

Physical Characters.—The colour is steel-grey to iron-black, and the streak black (or very dark brown); opaque. Brittle; $H=4$. The fracture is conchoidal, but in places sub-conchoidal to uneven, especially where the crystals are much intergrown close to the matrix.

Sp. gr. of the material analysed 5.047 at 22° .

Associations.—The matrix is a dirty yellow mixture of dolomite and a sealy talcose mineral, enclosing one or two crystals of pyrites and quartz and some massive tetrahedrite (?). On the free surfaces are two or three crystals of galena (cubo-octohedra with small $d\{110\}$) intimately associated with the crystals of tetrahedrite, and apparently formed at the same time. These crystals are partially embedded in white barytes, which, as shown by the cleavages, preserves its crystalline continuity over a considerable area. This barytes and some of the dolomite have crystallised around the tetrahedrite, and were the latest minerals to be formed; they present no natural faces, but only cleavage surfaces, through which the crystals of tetrahedrite project.

With the lens one or two minute crystals of what appeared to be copper-pyrites were observed on a crystal of tetrahedrite; but when the surface of the tetrahedrite crystals was illuminated with the aid of a Lieberkuhn

and examined under the microscope, minute yellow crystals were more often seen. The fractured surfaces of the tetrahedrite rarely showed a bright yellow tarnish due to a film of copper- or iron-pyrites.

Chemical Composition.—The result of the analysis was as follows (G. T. P.):—

				Atomic ratios.
Cu	...	30.56	.4842	6
Ag	...	15.26	.1425	
Sb	...	27.73	.2320	
As	...	trace		2.21
Fe	...	3.51	.0631	
Zn	...	trace		
Pb	...	0.05	.0002	.60
S	...	23.15	.7272	
		100.26		
Sp. gr.	...	5.047		

Weight used = 0.8911 gram, and 0.4447 gram for the sulphur determination. The atomic ratio of the total sulphur calculated for sulphides, on the assumption that iron is present as FeS, is .7247. After deducting $3(\text{Cu,Ag})_2\text{S.Sb}_2\text{S}_3$, the atomic ratios for the residual

$$\text{Sb} : (\text{Fe,Zn}) : \text{S} = .21 : .6 : .97,$$

which correspond very closely to the formula $6(\text{Fe,Zn})\text{S.Sb}_2\text{S}_3$. The combined formula is therefore the same as in the case of the Horhausen specimen :

$$[3(\text{Cu,Ag})_2\text{S.Sb}_2\text{S}_3] + \frac{1}{10}[6(\text{Fe,Zn})\text{S.Sb}_2\text{S}_3].$$

The above analysis resembles Rose's (see No. 2, p. 205) and the earlier analysis of Klaproth¹ of tetrahedrite from the Wenzel Mine, Wolfach, Baden.

(e) *Proposed new formula for Fahlerz (Tetrahedrite and Tennantite).*

$$3\text{R}'_2\text{S.R}'''_2\text{S}_3 + x[6\text{R}''\text{S.R}'''_2\text{S}_3],$$

where $\text{R}' = \text{Cu,Ag}$; $\text{R}'' = \text{Fe,Zn}$; $\text{R}''' = \text{Sb,As,Bi}$; and x is a small fraction, often $= \frac{1}{10}$ and $\frac{1}{5}$, but rising to $\frac{1}{2}$ in the case of the highly ferri-ferous tetrahedrite, "coppite."

The result of the analysis (p. 197) of the mineral from Dauphiné containing little iron or zinc served to substantiate the conclusion which had been arrived at from the analysis of binnite and the older analyses of tennantite and tetrahedrite of simple composition that the true formula for fahlerz proper is $3(\text{Cu,Ag})_2\text{S.}(\text{Sb,As})_2\text{S}_3$.

¹ *Beiträge*, 1807, IV, 71.

In the case of the last two analyses of specimens of less simple composition, if FeS and ZnS be taken as isomorphously replacing Cu_2S , the numbers obtained, like those of most analyses of tetrahedrite, correspond to a mixture of $3\text{RS.Sb}_2\text{S}_3$ and $4\text{RS.Sb}_2\text{S}_3$.

If, however, the above conclusion is accepted, that the true formula for the simple sulphantimonite of copper is $3\text{Cu}_2\text{S.Sb}_2\text{S}_3$, then the last two analyses serve to indicate in what way the iron and zinc enter into the composition of the more complex varieties of the mineral, for it is only necessary to deduct from the atomic ratios of the elements the whole of the Cu and Ag with part of the Sb, As and S to form $3(\text{Cu, Ag})_2\text{S.}(\text{Sb, As})_2\text{S}_3$, in order to see what ratio the (Fe, Zn) bears to the residual (Sb, As) and S.

As seen on pp. 200 and 202, application of this process to the last two analyses indicates that the Fe and Zn enter into the composition of the mineral as $6(\text{Fe, Zn})\text{S.Sb}_2\text{S}_3$, the group $6(\text{Fe, Zn})\text{S}$ and not $3(\text{Fe, Zn})\text{S}$ isomorphously replacing $3\text{Cu}_2\text{S}$.

The new formula receives its theoretical explanation in the suggestion which is tentatively put forward that in the crystallisation of the normal sulphantimonite of copper, sulphides of iron and zinc in small amount may be drawn into the composition of the mineral in the form $(\text{Fe, Zn})_6\text{S}_6.\text{Sb}_2\text{S}_3$, as the combination with sulphide of antimony most nearly approaching in structure to $\text{Cu}_6\text{S}_3.\text{Sb}_2\text{S}_3$. In fahlerz therefore $(\text{Fe, Zn})_6\text{S}_6$ is supposed to isomorphously replace Cu_6S_3 , owing to the predominating influence or "mass effect"¹ of the metallic atoms. The theory is thus an extension of the idea, which appears to be now gaining ground, that in many cases it is the number of atoms irrespective of their valency which is of importance in isomorphism² (*e.g.* the feldspars $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$; calcite and sodium nitrate).

(f) *Test of the new formula by reference to the results of previous analyses.*

The following eighteen analyses on which to test the new formula are arranged in order of date, beginning with those of Rose,³ from which the original 4 : 1 formula was deduced.

¹ Compare Penfield, *Amer. Journ. Sci.* 1896, II, 28; Abstract *Min. Mag.* XI, 275. *Ibid.* 1899, VII, 123; Abstract this No. p. 217.

² Hamberg, *Geol. För. Förh.* 1890, XII, 598; Penfield and Foote, *Amer. Journ. Sci.* 1897, L, 110.

³ Two out of Rose's seven analyses are not included, as they show intermixed matrix, and large percentages of both arsenic and antimony, the separation of which was by an imperfect method.

They are chosen for the most part as having been made on pure material and by good methods of analysis. As a rough test of the value of the analysis, in each case, to the atomic proportion of sulphur found is appended the atomic proportion of sulphur calculated to convert the other elements into sulphides ($\text{Cu}_2\text{S}, \text{FeS}, \text{Sb}_2\text{S}_3$ etc.).

After each analysis are given the atomic ratios of R'' (Fe, Zn), and of the residual R''' ($\text{Sb}, \text{As}, \text{Bi}$) and S left after deducting the whole of the copper and silver and part of the R''' and S to form $3(\text{Cu}, \text{Ag})_2\text{S} \cdot (\text{Sb}, \text{As})_2\text{S}_3$. According to the new formula, in a perfect analysis the atomic ratios of R'' and the residual R''' and S should be $\text{R}'' : \text{R}''' : \text{S} = 6 : 2 : 9$.

In the cases where the colour of the streak is mentioned, the analyses will be seen to confirm the suggestion made on p. 192 that in fahlerz the black streak is due to the presence of iron in larger amount than 3 per cent.

(1). *Tetrahedrite from Zilla, near Clausthal, Harz.*

H. Rose (*Pogg. Ann.* 1829, XV, 578). Tetrahedral crystals with copper-pyrites and galena. Streak, very dark red.

				Atomic ratios.
Cu	...	34.48	.5463	6
Ag	...	4.97	.0464	
Sb	...	28.24	.2363	2 + .392
Fe	...	2.27	.0408	
Zn	...	5.55	.0855	1.278
S	...	24.73	.7769	
			(Calc ^{d.} .7771)	6 + 1.864
<hr/>				
100.24				
<hr/>				

$$\text{Residual } \text{R}'' : \text{R}''' : \text{S} = 1.278 : .392 : 1.864 \\ = 6.5 : 2 : 9.5$$

corresponding to $6\text{RS} \cdot \text{R}_2\text{S}_3 + .5\text{RS}$.

$$\text{Approx. formula} : [3\text{R}_2\text{S} \cdot \text{Sb}_2\text{S}_3] + \frac{1}{5} [6\text{RS} \cdot \text{Sb}_2\text{S}_3].$$

(2). *Tetrahedrite from Wenzel Mine, Wolfach, Baden.*

Rose (*loc. cit.* p. 579). Crystals with barytes and galena on talcose gneiss. Streak, black.

				Atomic ratios.
Cu	...	25.23	.3997	6
Ag	...	17.71	.1653	
Sb	...	26.63	.2228	2 + .365
Fe	...	3.72	.0669	1.217
Zn	...	3.10	.0478	
S	...	23.52	.7389	6 + 1.844
			(Calc ^d . .7314)	
		99.91		

$$\text{Residual } R'' : R''' : S = 1.217 : .365 : 1.844 \\ = 6.6 : 2 : 10$$

corresponding to $6RS.R_2S_3 + .5RS_2$.

$$\text{Approx. formula : } [3R_2S.Sb_2S_3] + \frac{1}{5}[6RS.Sb_2S_3].$$

(3). *Tetrahedrite from Dillenburg, Nassau.*

Rose (*loc. cit.* p. 578). Tetrahedral crystals with copper-pyrites.
Streak, cherry-red.]

				Atomic ratios.
Cu	...	38.42	.6087	6
Ag	...	0.83	.0077	
Sb	...	25.27	.2115	2 + .355
As	...	2.26	.0304	
Fe	...	1.52	.0273	1.292
Zn	...	6.85	.1055	
S	...	25.03	.7864	6 + 1.655
			(Calc ^d . .8038)	
		100.18		

$$\text{Residual } R'' : R''' : S = 1.292 : .355 : 1.655 \\ = 7 : 2 : 9$$

corresponding to $6RS.R_2S_3 + R''$.

$$\text{Approx. formula : } [3R_2S.R_2S_3] + \frac{1}{5}[6RS.R_2S_3].$$

(4). *Tetrahedrite from Kapnik, Hungary.*

Rose (*loc. cit.* p. 577). Crystals with quartz, galena, iron-pyrites and blende. Streak, dark red.

				Atomic ratios.
Cu	...	37.98	.6017	6
Ag	...	0.62	.0058	
Sb	...	23.94	.2003	2+ .361
As	...	2.88	.0387	
Fe	...	0.86	.0155	1.262
Zn	...	7.29	.1123	
S	...	25.77	{ .8096 (Calc ^d . .7901)	6+1.996
			99.34	

$$\text{Residual } R'' : R''' : S = 1.262 : .361 : 1.996 \\ = 6.7 : 2 : 10.7$$

corresponding to $6RS.R_2S_3 + .7RS_2$.

Approx. formula: $[3R_2S.R_2S_3] + \frac{1}{5}[6RS.R_2S_3]$.

(5). *Argentiferous Tetrahedrite from Freiberg, Saxony.*

Rose (*loc. cit.* p. 579). Tetrahedral crystals with galena, copper-pyrites, red-silver, blende and quartz. Streak, black.

				Atomic ratios.
Cu	...	14.81	.2346	6
Ag	...	31.29	.2921	
Sb	..	24.63	.2061	2+ .348
Fe	...	5.98	.1076	1.285
Zn	...	0.99	.0152	
S	...	21.17	{ .6651 (Calc ^d . .6852)	6+1.577
			98.87	

$$\text{Residual } R'' : R''' : S = 1.285 : .348 : 1.577 \\ = 7 : 2 : 9$$

corresponding to $6RS.Sb_2S_3 + R''$.

Approx. formula: $[3R_2S.Sb_2S_3] + \frac{1}{6}[6RS.Sb_2S_3]$.

(6). *Tetrahedrite from Clausthal, Harz.*

Schindling (*Neues Jahrb. f. Min.* 1856, 335). Tetrahedral crystals, coated with copper-pyrites.

				Atomic ratios.
Cu	...	33.145	.5251	6
Ag	...	5.135	.0479	
Sb	...	28.520	.2387	2 + .499
Fe	...	2.730	.0491	1.446
Zn	...	5.775	.0890	
S	...	25.655	.8060	6 + 2.446
			(Calc ^d . .7826)	
		<hr/>		
		100.960		

$$\text{Residual } R'' : R''' : S = 1.446 : .499 : 2.446 \\ = 5.8 : 2 : 9.8$$

corresponding to $6RS.Sb_2S_3 + .8S$.

$$\text{Approx. formula: } [3R_2S.Sb_2S_3] + \frac{1}{4}[6RS.Sb_2S_3].$$

(7). "*Coppite*" from *Val di Frigido, Tuscany*.

Bechi (D'Achiardi *Min. Tosc.* 1873, II, 341, from *Cont. Atti Accad. Georgofili, Florence*, 1863, X, 203). Compact and homogeneous. Sp. gr. 4.713.

				Atomic ratios.
Cu	...	30.10	.4769	6
Sb	...	29.61	.2478	2 + 1.116
Fe	...	13.08	.2352	2.959
S	...	27.01	.8486	6 + 4.674
			(Calc ^d . .8453)	
		<hr/> 99.80		

$$\text{Residual } R'' : R''' : S = 2.959 : 1.116 : 4.674 \\ = 5.3 : 2 : 8.4$$

corresponding to $6FeS.Sb_2S_3 - .6RS$.

$$\text{Approx. formula: } [3Cu_2S.Sb_2S_3] + \frac{1}{2}[6FeS.Sb_2S_3].$$

(8). *Mercurial Tetrahedrite* from *Moschellandsberg, Rhenish Bavaria*.

Oellacher (Sandberger, *Neues Jahrb. f. Min.* 1865, 596). Crystals with copper-pyrites. Streak, black. Sp. gr. 5.095.

				Atomic ratios.
Cu	...	32.19	.5100	6
Sb	...	23.45	.1962	2 + .446
As	...	0.31	.0041	
Bi	...	1.57	.0076	
Fe	...	1.41	.0254	
Zn	...	0.10	.0015	1.390
Hg	...	17.32	.0873	
Co	...	0.23	.0040	
S	...	21.90	.6880	
Gangue	...	1.39	(Calc ^d .6819)	6 + 2.095
			99.87	

$$\text{Residual } R'' : R''' : S = 1.390 : .446 : 2.095 \\ = 6.2 : 2 : 9$$

corresponding to $6RS.R_2S_3$.

$$\text{Approx. formula : } [3Cu_2S.R_2S_3] + \frac{1}{4}[6RS.R_2S_3].$$

(9). *Tetrahedrite from De Soto Mine, Star City, Nevada.*

Burton (*Amer. Journ. Sci.* 1868, XLV, 37). Massive, with blende and pyrites. Sp. gr. 5.00.

				Atomic ratios.
Cu	...	27.40	.4340	6
Ag	...	14.59	.1362	2 + .408
Sb	...	27.35	.2289	
Fe	...	4.27	.0768	
Zn	...	2.31	.0356	
S	...	24.35	.7650	6 + 2.049
			(Calc ^d .7409)	
Insol.	...	0.35		
			100.62	

$$\text{Residual } R'' : R''' : S = 1.183 : .408 : 2.049 \\ = 6 : 2 : 10$$

corresponding to $6RS.R_2S_3 + S$.

$$\text{Approx. formula : } [3R_2S.Sb_2S_3] + \frac{1}{5}[6RS.Sb_2S_3].$$

(10). "*Julianite*" from *Rudelstadt, Silesia*.

Websky (*Zeits. Deutsch. geol. Ges.* 1871, XXIII, 486). Small cubo-dodecahedra in calcite. Sp. gr. 5.12.

				Atomic ratios.
Cu	...	52.298	.8286	6
Ag	...	0.538	.0050	
Sb	...	1.421	.0118	1.708
As	...	16.782	.2255	
Fe	...	0.787	.0142	.102
S	...	26.503	.8326	5.993
			(Calc ^{d.} .7870)	
<hr/>				
98.329				

The numbers correspond approximately to $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$. The correspondence is more exact if, as is most probable from the imperfect method of analysis (fusion with nitre and sodium carbonate), the loss in the analysis is due to loss of arsenic.

This analysis is given as one of the few made on material of comparatively simple composition.

(11). "*Aphthonite*" from *Gärdsjö, Wernland, Sweden*.

Nilson (*Zeits. Kryst. Min.* 1877, I, 417). Massive, with small veins of copper-pyrites. Streak, dark brownish red.

				Atomic ratios.
Cu	...	41.06	.6505	6
Ag	...	6.16	.0575	
Sb	...	26.85	.2247	1.904
Fe	...	0.95	.0171	.152
Zn	...	0.71	.0109	
S	...	23.56	.7462	6.27
			(Calc ^{d.} .7090)	
<hr/>				
99.29				

The numbers correspond very closely with the formula $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$.

(12). *Fahlerz* from *Kahl, near Bieber, in Hesse*.

Mutschler (Sandberger, *Neues Jahrb. f. Min.* 1877, 275). Sp. gr. 4.75.

				Atomic ratios.
Cu	...	36.3	.5751	6
Ag	...	0.5	.0050	
Sb	...	24.9	.2084	2+ .516
As	...	2.6	.0349	
Fe	...	3.6	.0648	1.475
Zn	...	4.5	.0693	
Co	...	0.5	.0085	
S	...	25.9	{ .8137	6+2.415
			{ (Calc ^d . .7974)	
<hr/>			98.8	

$$\text{Residual } R'' : R''' : S = 1.475 : .516 : 2.415 \\ = 5.7 : 2 : 9.3$$

corresponding to $6RS.R_2S_3$.

Approx. formula : $[3R_2S.R_2S_3] + \frac{1}{4}[6RS.R_2S_2]$.

(13). *Fahlerz from Huallanca, Peru.*

Comstock (*Amer. J. Sci.* 1879, XVII, 401). Large tetrahedral crystals. Sp. gr. 4.7.

				Atomic ratios.
Cu	...	39.09	.6193	6
Ag	...	3.86	.0360	
Sb	...	9.06	.0758	2+ .354
As	...	13.49	.1812	
Fe	...	5.46	.0982	1.201
Zn	...	2.14	.0330	
S	...	26.74	{ .8401	6+1.693
			{ (Calc ^d . .8453)	
<hr/>			99.84	

$$\text{Residual } R'' : R''' : S = 1.201 : .354 : 1.693 \\ = 6.7 : 2 : 9.6$$

corresponding to $6RS.Sb_2S_3 + .6RS$.

Approx. formula : $[3R_2S.R_2S_3] + \frac{1}{5}[6RS.R_2S_3]$.

(14). *Fahlerz from Kapnik, Hungary.*

Hidegh (*Tsch. Min. Mitth.* 1879, II, 350—8). Crystals with blende. Sp. gr. 4.91 (compare No. 4 above).

				Atomic ratios.
Cu	...	37.83	.5993	6
Ag	...	1.32	.0123	
Sb	...	24.21	.2026	
As	...	2.88	.0444	2 + .423
Fe	...	0.94	.0169	1.262
Zn	...	7.25	.1117	
S	...	25.31	.7951	6 + 1.801
			(Calc ^d . .8049)	
<hr/>			99.74	
<hr/>				

$$\text{Residual } R'' : R''' : S = 1.262 : .423 : 1.801 \\ = 6 : 2 : 8.5$$

corresponding to $6RS.R_2S_3$.

$$\text{Approx. formula: } [3R_2S.R_2S_3] + \frac{1}{5} [6RS.R_2S_3].$$

(15). *Tennantite from Szászka, Hungary.*

Hidegh (*loc. cit.*). Dodecahedral crystals associated with redruthite.
Sp. gr. 4.92.

				Atomic ratios.
Cu	...	53.60	.8491	6 7
Ag	...	0.08	.0008	
Sb	...	0.10	.0008	1.736 2
As	...	19.11	.2567	
Fe	...	0.39	.0070	.05
S	...	25.98	.8162	5.76 6.5
			(Calc ^d . .8181)	
<hr/>			99.26	
<hr/>				

$$\text{Approx. formula: } 3Cu_2S.As_2S_3 + \frac{1}{2}Cu_2S \text{ (redruthite).}$$

(16). *Fahlerz from Herrengrund, Hungary.*

Hidegh (*loc. cit.*) Imperfect crystals, somewhat altered. Sp. gr. 4.77.

				Atomic ratios.
Cu	...	39.81	.6307	6
Ag	...	0.05	.0005	
Sb	...	22.82	.1909	2 + .421
As	...	4.75	.0638	
Fe	...	4.75	.0854	1.023
Zn	...	1.44	.0222	
S	...	25.75	.8090	6 + 1.690
			(Calc ^d . .8052)	
<hr/>				
99.37				
<hr/>				

$$\text{Residual } R'' : R''' : S = 1.023 : .421 : 1.690$$

$$= 5 : 2 : 8$$

corresponding to $6RS.R_2S_3 - RS$.

$$\text{Approx. formula: } [3Cu_2S.R_2S_3] + \frac{1}{5}[6RS.R_2S_3].$$

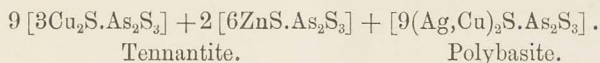
(17). *Tennantite from Mollie Gibson Mine, Aspen, Colorado.*

Penfield (*Amer. Journ. Sci.* 1892, XLIV, 18). Massive; intermixed with polybasite, from which it only slightly differs in colour. Sp. gr. 4.56.

				Atomic ratios.
Cu	...	35.72	.5659	6
Ag	...	13.65	.1274	
Sb	...	0.13	.0011	2.007
As	...	17.18	.2308	
Fe	...	0.42	.0075	.985
Zn	...	6.90	.1063	
Pb	...	0.86	.0042	.036
S	...	25.04	.7867	6.808
			(Calc ^d . .8125)	
<hr/>				
99.90				
<hr/>				

This analysis is introduced as being one of the very few which agree closely with the 4 : 1 formula, in this case $3Cu_2S.ZnS.Sb_2S_3$. The result of the analysis can only be made to agree with the new 3 : 1 formula, either by supposing the zinc to be present as blende, or, as is more probable from the mode of occurrence of the mineral, by supposing that

the material analysed contained admixed polybasite, as shown in the following formula:—



Taking the atomic proportion of copper and silver in the polybasite to be 1 : 3, as given by Penfield's analysis (*loc. cit.*), the atomic proportion of these elements in the above formula is about 9 : 2, which is in fairly close agreement with the results of the analysis.

(18). *Fahlerz from Clausthal, Harz.*

Fraatz (W. Hampe, *Chem.-Zeit.* 1893, XVII, p. 1691). Crystals coated with copper-pyrites, but the selected material appeared to be perfectly homogeneous under the microscope. The mean of two closely agreeing analyses is—

				Atomic ratios.
Cu	...	35.645	.5642	6
Ag	...	3.865	.0314	
Sb	...	28.63	.2394	2 + .412
Fe	...	2.86	.0422	1.247
Zn	...	5.29	.0815	
S	...	24.72	{ .7725 (Calc'd. .7806)	6 + 1.7826
<hr/>				
100.01				

$$\text{Residual R'' : Sb : S} = 1.247 : .412 : 1.782$$

$$= 6 : 2 : 8.65$$

corresponding to $6\text{RS.Sb}_2\text{S}_3$.

$$\text{Approx. formula : } [3\text{R}_2\text{S.Sb}_2\text{S}_3] + \frac{1}{5} [6\text{RS.Sb}_2\text{S}_3].$$

In support of the new formula particular attention may be drawn to the analyses of Rose (Nos. 1-5), to the analysis of "coppite" (No. 7) in which the percentage of iron is as high as 13, and to the analysis of Fraatz (No. 18) which is one of the most recent analyses of tetrahedrite made on pure crystallised material.

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